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CONTENTS — INHOUD

Page
Bladsy

THE USE OF DILITURIC ACID IN THE DETERMINATION OF POTASSIUM
by R. E. Press and K. A. Murray 17

THE UNSATURATED NATURE OF THE *CYCLO*PROPANE RING
A Note on Some Light Absorption Data
by G. W. Perold 22

FERTILISER STUDIES WITH TOBACCO PLANTS USING RADIO-PHOSPHORUS-LABELLED SUPERPHOSPHATE
Part III.
by H. L. Pearse and L. H. Stein 25

THE NITRIC ACID OXIDATION OF COAL
Part IV. Application of the Graphical-Statistical Method to the Interpretation of the Investigations of the Nitrohumic Acids
by B. L. van Duuren 31

THE CALIBRATION OF A STORMER VISCOSIMETER WITH SPECIAL REFERENCE TO TURBULENT FLOW CONDITIONS
by P. J. van der Walt and A. M. Fourie 36

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THE USE OF DILITURIC ACID IN THE DETERMINATION OF POTASSIUM

by

R. E. PRESS and K. A. MURRAY

OPSOMMING

Kalium word volgens 'n jodometriese-metode bepaal waarvoor dilituursuur as presipiteermiddel gebruik word. Die oormaat suur word as kopersout gepresipiteer, en die oormaat koper deur terugtitrasie bepaal. Vir kaliumhoeveelhede binne die grense 35 mg. tot 10 mg., is die noukeurigheid vir 'n duplikaatbepaling ongeveer 1·0 mg. So min as 0·1 mg. kalium gee 'n presipitaat. Katione soos litium en natrium, en anione soos chloried, fosfaat, sulfaat, nitraat, ens. wat koperbepalinge nie steur nie, kan teenwoordig wees.

'n Klein hoeveelheid natriumione verseker noukeuriger resultate.

SUMMARY

Potassium is determined by an iodometric procedure involving the use of dilituric acid as a potassium precipitant, the determination of the excess acid by precipitation of the copper salt and back titration of the excess copper. Potassium may be determined in the range 10—35 mg. to within 1·0 mg. on a duplicate determination. As little as 0·1 mg. of potassium can be detected by the formation of a precipitate. Sodium, lithium and anions which do not interfere with a copper titration, *e.g.* chloride, phosphate, sulphate, nitrate, etc., may be present. A small concentration of sodium ions is necessary for accurate results.

Dilituric acid appears to have been little investigated as a quantitative method for potassium determination. It was first reported as a precipitant for potassium by Fredholm[1] in 1936, and was then variously investigated by Dermer and Dermer[2], and Redeman and Nieman[3], who published results on the solubilities of its various salts. The only reported use of the reagent as a measure of potassium is by De Graaf and Noyons[4], who used pure potassium chloride solutions and weighed the precipitate formed therefrom.

Dilituric acid has been the subject of investigation by organic chemists[5], but little work has been done on its physico-chemical properties. It is a strong acid, as shown by conductivity measurements[6], and its ion has a strong yellow colour. The alkali salts are stable in the presence of mineral acids but are dissolved by strong alkalies to form the salt of the dibasic acid.

ANALYTICAL PROCEDURE FOR POTASSIUM DETERMINATION

Reagents required

Dilituric acid, 0·05 N.

The acid is prepared by the procedure reported in Organic Syntheses[7] and recrystallized from water. It is made up to approximately 0·05 N. by titration with sodium hydroxide using phenol phthalein as indicator. Potassium dilituratе is added to the solution so as to saturate it and the clear supernatant liquid or the solution after filtering is used.

Copper sulphate, 1·0 N.

Copper sulphate is dissolved in water and a few drops of sulphuric acid are added.

Wash solution.

This is a saturated solution of potassium dilituratе freshly prepared.

The potassium dilituratе used above is prepared by precipitation of the salt from excess dilituric acid and potassium chloride. The precipitate is washed well with water and dried at 80°C. It keeps well.

Standard sodium thiosulphate, 0·1 N.

Procedure.—5 ml. of the potassium solution, containing less than 35 mg. of potassium is added to 20 ml. of dilituric acid. The solution and precipitate are mixed occasionally and filtered through a sintered glass Gooch adapter (Jena grade No. 4), and the beaker and precipitate washed with 10 ± 0·5 ml. of wash solution.

To the filtrate (about 35 ml.) is added 2 ml. of copper sulphate solution, with constant stirring. The precipitate and solution are mixed occasionally, especially in cases of high potassium concentrations. The solution is filtered through a sintered glass adapter as before and washed with about 10 ml. of water.

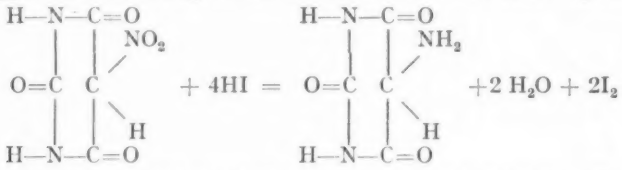
The filtrate is neutralized with ammonium hydroxide and the slight precipitate of copper hydroxide dispelled with a few drops of acetic acid. The copper is then titrated in the usual manner using potassium iodide and sodium thiosulphate. Thiocyanate may be added at the endpoint.

Concurrently with the above a blank on distilled water is done. The potassium is then equivalent to twice the difference between the determination and the blank (*cf.* section iv which follows).

FACTORS AFFECTING ACCURACY

(i) pH of final titration solution

In the titration of the copper filtrate the pH should be adjusted as directed so as just to prevent the precipitation of copper hydroxide. This is not only desirable for the copper titration, but prevents interference from the following reaction[8].



which occurs in strongly acid solution in the presence of iodide ions. (The dilituratе ions are present due to the slight solubility of copper dilituratе.)

TABLE I

SHOWING THE INFLUENCE OF PRECIPITATION TIME FOR TWO DIFFERENT SINTERED GLASS FILTERS

Time (*hours*)	ml. 0·1 N. $Na_2S_2O_3$	
	Coarse filter No. 2	*Fine filter No.* 4
0·5	8·45	5·40
1·0	8·40	5·16
1·5	8·35	—
2·0	—	5·12
2·5	8·32	—
3·0	8·30	5·08
4·0	8·25	5·09
5·0	—	5·11
6·0	—	5·12
8·0	8·24	5·10
24·0	8·24	5·00

(ii) **Time allowed for precipitation**

Table I shows the effect of varying the time before filtration of the copper dilituratе, from a solution of dilituric acid to which excess copper sulphate had been added. The effect of changing to a finer grade of sintered glass filter is also shown. Thus a time lapse of about 2·5 to 3 hours is satisfactory using a No. 4 (Jena) sintered glass filter. Stirring of the precipitate and solution every quarter- to half-hour considerably improves the concordance of the results.

Similar conditions apply to the potassium precipitation but are less critical.

(iii) **Wash solution**

The variance ratio from seven determinations using an arbitrary volume of distilled water with which to wash the potassium precipitate, and seven where washing was carried out as indicated (under "determination"), is $\frac{21{\cdot}85}{7{\cdot}43} = 2{\cdot}98$ and F for 7 and 7 degrees of freedom at the 10 per cent level is 2·78. Thus it is considered advantageous to use this latter method of washing.

In the case of the copper dilituratе precipitate the volume of wash water does not significantly affect the accuracy; however, about 10 ml. should be used.

(iv) **Effect of sodium ions**

A series of potassium determinations in solutions containing various amounts of sodium were made. The slopes b of the lines which were obtained from the above series of determinations are reported in Table II, Column 2 and have been calculated assuming the potassium value (x ml. 0·1 M. K^+ in 5 ml. of solution), to be accurately known as compared with the titration value (y ml. 0·1 N. $Na_2S_2O_3$) ($y = bx + a$, a = blank).

TABLE II

EFFECT OF SODIUM CONCENTRATION ON STOCHEIOMETRY OF REACTION

Sodium concentration ml. 0·1 M./5 ml.	*Slope* b	$\hat{\sigma}_y$	$\hat{\sigma}_b$	*Degrees of freedom*	"t" *at* 5%	$\frac{0{\cdot}5-b}{\hat{\sigma}_b}$
0·00	0·456	0·084	0·011	5	2·57	3·7
0·25	0·490	0·040	0·0067	4	2·77	1·5
0·75 = 1·7 mg.	0·468	0·076	0·0116	4	2·77	2·75
2·50	0·498	0·051	0·0086	4	2·77	0·23
5·00	0·490	0·045	0·0080	4	2·77	1·25
10·00	0·495	0·043	0·0070	4	2·77	0·71
12·50	0·490	0·065	0·0093	5	2·57	1·06
13·75	0·488	0·093	0·016	4	2·77	0·75

Column 7 of Table II gives values for a "Student's" t test on the slope, to show variation from 0·5, the stoicheiometric value. The slope of 0·5 is due to the different

equivalents of copper in the thiosulphate titration and in the precipitation reaction. The dilituric acid acts as a monobasic acid with respect to the potassium and the copper in the precipitation reactions.

It will be seen that stocheiometric results are obtained if sodium is present in concentrations greater than about 2 mg. per 5 ml. sample. If it is not present it can easily be added to the potassium sample.

(v) **Accuracy**

A series of potassium determinations were done by the authors (a) and two chemistry honours students (b, c) who had no previous experience in the method. Table III shows the results of such experiments. In all cases there is no significant deviation from stoicheiometry and the standard deviations are comparable as shown by Bartlett's test. Thus it can be stated that no previous experience of the method is needed to obtain satisfactory results.

TABLE III

COMPARISON OF RESULTS OF DIFFERENT EXPERIMENTERS

Experimenter	*Slope b*	$\hat{\sigma}_y$	$\hat{\sigma}_b$	*Degrees of freedom*	"t" *at* 5%	$\frac{0{\cdot}5-b}{\hat{\sigma}_b}$
a	0·5065	0·054	0·00584	8	2·31	1·11
b	0·4855	0·096	0·014	4	2·77	1·00
c	0·4905	0·037	0·0055	4	2·77	1·7

To test for the homogeneity of the variance in the above we calculate

$$\frac{B}{C} = \frac{\Sigma n.\ \log_e \{\text{pooled } (\hat{\sigma}_y)^2\} - \Sigma n.\ \log_e (\hat{\sigma}_y)^2}{1 + \frac{\Sigma(1/n) - 1/\Sigma n}{3\,(K-1)}}$$

$$= \frac{16 \log_e 0{\cdot}0041 - (-91{\cdot}88)}{1 + \frac{0{\cdot}625 - 0{\cdot}0625}{3\,(3-1)}}$$

$$= 3{\cdot}64$$

The critical 10 per cent. level for χ^2 for 2 degrees of freedom is 4·61. Thus it can be said that there is no significant variation in the precision of the various analysts.

(vi) **Precision**

A pooled estimate of $\hat{\sigma}_y$ from Tables II and III gives a value of 0·065 ml. of 0·1 N. sodium thiosulphate, (from a population with 50 degrees of freedom). Thus if the determinations of the blank and the unknown are done in duplicate, the value of the unknown in milligrams can be relied on to $\pm$ 1·0 mg. with a certainty of 95 per cent.

INTERFERENCES

Rubidium, caesium and ammonium ions interfere but not sodium and lithium. Ions from other groups have not been investigated but it is probable that ions from Group I will not interfere. Anions which do not interfere with a copper titration may be present. Determinations in the presence of sodium, lithium, sulphate and phosphate are shown in Table IV.

TABLE IV

EFFECT OF VARIOUS IONS ON POTASSIUM DETERMINATION

(Concentrations in ml. 0·1 M. solution/5 ml. sample). ("t" = 2·3 at 5 per cent and 8 degrees of freedom.)

Concentration of salts added				Potassium found 2(titration — blank) mean of 5 each	$\hat{\sigma}$ (difference of means)	$K_{found} - K_{present}$ / $\hat{\sigma}$(difference of means)
Na_2HPO_4	NaCl	Li_2SO_4	KCl			
2·5	2·5	—	2·271	2·268	0·029	0·1
—	2·5	2·5	2·018	2·056	0·0346	1·1

The authors thank Professor H. Stephen for his interest and encouragement.

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THE UNSATURATED NATURE OF THE *CYCLO*PROPANE RING

A NOTE ON SOME LIGHT-ABSORPTION DATA

by

G. W. PEROLD

OPSOMMING

Die ultraviolet-absorpsiespektra van vyf nuwe isomeriese monometiel-substitusieprodukte van *trans* 2-feniel-*siklo*propaankarboksamied is bepaal. Aan die hand hiervan word afgelei dat die *siklo*propaanring in sekere gevalle uitdruklike konjugasievermoë openbaar. Die oorsaak hiervan word toegeskryf aan die vermoë van die 1,2-koolstof-koolstofbinding om in daardie gevalle 'n hoë mate van dubbelbindingskarakter te ontwikkel.

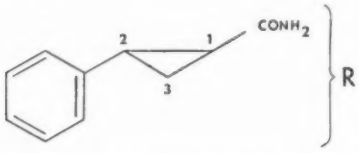
SUMMARY

The ultra violet absorption spectra of five new isomeric mono-methyl substitution products of *trans* 2-phenyl-*cyclo*propanecarboxamide have been determined. The results lead to the conclusion that the *cyclo*propane ring can in some cases exhibit pronounced conjugative properties. This is ascribed to the ability of the 1,2 carbon-carbon bond to develop a high degree of double bond character in such cases.

The *cyclo*propane ring in many ways behaves as an unsaturated system[1]. Thus, while the system is reasonably stable towards potassium permanganate and ozone[2] the strain present in the three-carbon ring is manifested by its ready rupture, on catalytic hydrogenation or by the addition of halogens or halogen hydrides, with the formation of open-chain compounds.

In connection with other studies[3] carried out in this laboratory, five isomeric *trans-x*-methyl-2-phenyl-cyclopropanecarboxamides were obtained from the reaction of ethyl diazoacetate[4] with the five isomeric monomethylstyrenes. As light-absorption measurements afford insight into the fine structure of many organic compounds, it was of some interest to investigate the nature of the *cyclo*propane system by these means. The ultra violet absorption spectra of these compounds were therefore determined and were found to yield interesting information on the state of unsaturation prevailing in the *cyclo*propane ring in these substances.

The absorption curves obtained for the five *trans cyclo*propane amides



I, R = *o*-Me
II, R = 2-Me
III, R = 3-Me
IV, R = *m*-Me
V, R = *p*-Me,

as well as for the unsubstituted methyl *trans*-2-phenyl-*cyclo*propanecarboxylate(VI)[2] are reproduced in Figure 1, while the relevant data are summarised in Table I.

TABLE I

Absorption maxima and minima

mμ/log ε

	max.	*min.*	*max.*	*max.*	*min.*	*max.*
I	—	250/2·32	—	266/2·55	—	—
II	—	256/2·29	258/2·36	264/2·29	—	—
III	221/4·03	250/2·30	260/2·53	266/2·59	270/2·35	274/2·48
IV	225/3·96	252/2·31	—	270/2·61	275/2·47	278/2·50
V	226/4·12	254/2·44	265/2·67	270/2·75	276/2·53	278/2·64
VI	221/4·01	250/2·33	260/2·49	265/2·52	270/2·28	273/2·39
VII	228/4·04	255/2·75	—	272/2·94	278/2·83	280/2·86

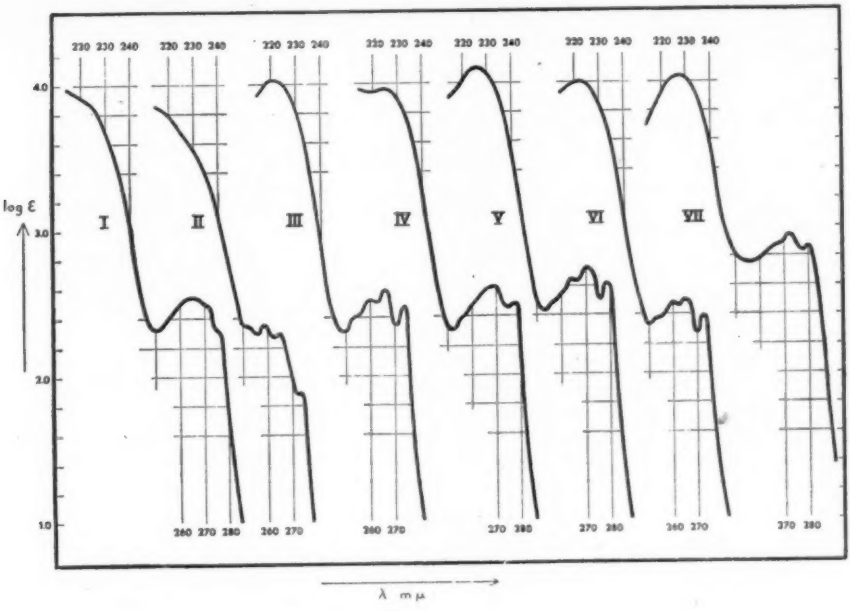


FIG. 1

The spectral curves show general similarity and may all be considered to consist of two parts, viz. the low intensity bands (log ϵ *ca.*2·5) in the region of *ca.* 260-278 mμ and the high intensity absorption (log ϵ *ca.*4) in the 221-226 mμ region. The low intensity bands may be ascribed to the aromatic nucleus, while the high intensity absorption in the further ultra violet may be considered to reflect the absorption due to a conjugated amide or ester group. Comparison of the ultra violet spectrum of benzoic acid (Fig. 1, VII) with that of benzene or toluene [5] illustrates this correlation. In the 2-aryl-*cyclo*propanecarboxylic acid series the aromatic absorption is depressed in intensity, with reference to benzoic acid as standard, while the high absorption peak shows equal absorption but has undergone a hypsochromic shift.

It will now be observed (Fig. 1) that in the case of the unsubstituted ester (VI) as well as for the 3-, *m*- and *p*-Me-amide derivatives (III-V) the high intensity peak is clearly developed while it does not appear in the case of the *o*- and 2-Me-amides (I-II). This suggests that the conjugation of the aromatic nucleus with the carbonyl group through the *cyclo*propane ring, apparent in the set of compounds first mentioned, is either strongly hindered or entirely destroyed by the presence of a methyl group substituted in the *o*- and 2-positions.

As the conjugation is not destroyed by the methyl group substituted in position 3 of the *cyclo*propane ring, it seems that this ring does not as a whole function as an unsaturated group, but that the unsaturation in these instances resides only in the two carbon atoms, 1 and 2, directly linking the aromatic and carbonyl groups. This becomes acceptable on the assumption that the unsaturation in the *cyclo*propane ring is in this case due to a type of hyper-conjugation.* The bond angle deformation resulting from the closing of the three-carbon ring may impose sufficient strain to

*Although a strictly formulated hyper-conjugation has been denied existence in the case of ≡C-H groups [6], we prefer in this case still to apply the general conception of hyperconjugation in a qualitative manner.

allow the development of predominantly double bond character for the bond in the 1,2 position, the site of the unsaturation being determined by the influence of the aromatic and carbonyl substituents. This would entail a concomitant weakening of the carbon-hydrogen bonds at carbon atoms 1 and 2. Where, however, one of these hydrogen atoms is substituted by a methyl group, as in the 2-methyl derivative, or is under the direct steric influence of a closely situated *and* rigidly held group, as in the *o*-methyl derivative, the mutability of these bonds is restricted. Development of a high degree of double bond character between carbon atoms 1 and 2 is then hindered, so that the through-conjugation from the aromatic to the carbonyl group is interrupted. The absence of the typical peak in the further ultra violet spectrum of dihydrocinnamic acid[7] provides supporting evidence.

It is therefore suggested that the unsaturation of the *cyclo*propane ring, deduced from the ultra violet spectra of the 2-phenyl-*cyclo*propanecarboxyl derivatives noted, is due to the development of a high degree of double bond character for the bond between the 1- and 2-carbon atoms of the *cyclo*propane ring only.

As a corollary to the data given in Table 1, it will be noticed that the ultra violet absorption spectra of the *trans-x*-methyl-2-phenyl-*cyclo*propanecarboxamides are well suited to serve for determining the position of the methyl substituent, and thus to characterise the isomeric methylstyrenes from which they are readily obtained. Such an application has already proved of value in a study reported elsewhere*.

EXPERIMENTAL

Methyl *trans*-2-phenyl-*cyclo*propanecarboxylate[2] and the five *trans-x*-methyl-2-phenyl-*cyclo*propanecarboxamides[3] were prepared as noted. In view of the somewhat unexpected nature of the spectral curve obtained for *trans*-2-methyl-2-phenyl-*cyclo*propanecarboxamide, the preparation of this compound from α-Me-styrene was repeated *in toto*, yielding however the identical product with exactly the same melting point and absorption spectrum.

The spectra were obtained in ethanol solution, using both the Beckman DU and Zeiss Opton spectrophotometers.

Thanks are expressed to the Director of the National Chemical Laboratory of the C.S.I.R., Pretoria, for the use of their Beckman instrument, to Mr. R. P. Badenhorst of this laboratory for the preparation of the illustration, and to the Manager, Scientific and Research Department, ISCOR, for permission to publish this note.

Research Laboratory,
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ISCOR,
Pretoria.

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FERTILIZER STUDIES WITH TOBACCO PLANTS USING RADIOPHOSPHORUS-LABELLED SUPERPHOSPHATE. PART III.

by

H. L. PEARSE and L. H. STEIN

OPSOMMING

Deur gebruikmaking van radioaktiewe superfosfaat is die effek van herhaalde toediening van fosfatiese kunsmis tot tabakplante op twee tipes grond bestudeer. Daar is bevind dat 'n toediening van 800 lb./morg van 'n 2N.12P.6K mengsel voldoende is en beter is as drie agtereenvolgende toedienings van een derde hierdie hoeveelheid. Drie toedienings van die volle hoeveelheid het die opname van fosfaat slegs effens verbeter.

SUMMARY

Utilising radioactive superphosphate, the effect of successive applications of phosphatic fertilizer on tobacco plants, has been studied on two soil types. A 800 lb./morgen application of a 2N.12P.6K mixture has been found to be adequate, and is better than three successive dressings of one-third this amount. Three dressings of 800 lb./morgen improved the uptake of phosphate only slightly.

In continuation of earlier work[1,2] on the absorption of phosphorus by tobacco the effect of successive applications of phosphatic fertilizer during the growth of the crop has been investigated further. In addition to a repetition of the previous treatments, three times the normal amount of phosphate was supplied in split applications and, in the attempt to ensure that growth was not unduly limited by nitrogen, twice the amount formerly used was applied. The work has also been expanded to embrace two different soil types.

MATERIALS

The superphosphate used was again prepared at the Research Department of Messrs. African Explosives and Chemical Industries, Ltd. at Modderfontein. In order to obtain the requisite quantity, it was necessary to prepare two batches. Nitrogen and potassium were however not incorporated at this stage, but were applied independently just prior to planting as ammonium sulphate and muriate of potash. Analysis of the two batches of superphosphate gave the following results:—Total P_2O_5, 20·3 and 20·8 *per cent.*, water soluble P_2O_5, 19·3 and 19·6 *per cent.*, and specific activity 829 and 814 μrd per mg. P_2O_5 on the 5th November, 1952.

The plants used were again of the Orinoco type Yellow Mammoth variety and were grown on plots at the Central Tobacco Research Station. The plants were 12 weeks old when transplanted, and the plots were on a black Noritic turf soil and on a red clay alluvial soil.

EXPERIMENTAL

A randomised block layout similar to that used in previous experiments was adopted, consisting of four replications of four treatments. On the black soil, four rows were treated with superphosphate equivalent to that contained in a dressing of 800 lb. per morgen of a 4N.12P.6K mix as treatment P. Treatment 3 × P/3 was one-third of this amount applied prior to planting and two similar amounts applied four weeks and eight weeks after planting. Treatment 3 × P was similar, except that the full amount was given at each application and the final dosage was thus three times that of the standard P treatment. Four control rows, treatment C, received no phosphatic fertilizer. Nitrogen and potassium as ammonium sulphate and potassium chloride respectively were applied to all plots before planting in quantities equivalent to that of an application of 800 lb. per morgen of a 4N.6K mixture.

TABLE I

Series	Days after planting	Treatment	Black Soil				Red Soil			
			Dry weight g.	mg. P_2O_5 per g. dry wt.	mg. Fert. P_2O_5 per g. dry wt.	Fert. P_2O_5 / Total P_2O_5 %	Dry weight g.	mg. P_2O_5 per g. dry wt.	mg. Fert. P_2O_5 per g. dry wt.	Fert. P_2O_5 / Total P_2O_5 %
1	13	P	4·88	7·67	1·48	19·25	4·65	7·90	1·30	16·40
		P/3	4·88	6·50	0·63	9·64	4·27	6·46	0·53	8·16
		P	5·45	8·10	1·71	21·14				
		C	5·26	4·58	—	—	3·39	6·28	—	—
2	27	P	19·9	6·09	3·63	59·69	17·5	6·55	3·60	54·98
		P/3	13·0	5·46	1·80	32·96	14·8	6·53	2·03	31·13
		P	19·5	6·00	3·23	53·86				
		C	12·0	5·47	—	—	11·5	5·86	—	—
3	41	P	104·2	5·74	2·54	44·16	123·2	5·95	1·97	33·18
		2×P/3	83·6	5·70	1·26	22·11	101·9	6·01	1·02	16·95
		2×P	96·3	5·87	2·49	42·47				
		C	65·5	5·68	—	—	71·6	5·76	—	—
4	55	P	251·1	5·35	1·73	32·37	249·1	5·82	1·78	30·53
		2×P/3	210·8	5·46	1·04	19·08	237·3	6·03	0·94	15·59
		2×P	227·6	5·66	1·86	32·92				
		C	171·9	5·37	—	—	198·8	5·88	—	—
5	69	P	612·9	5·04	1·24	24·63	582·3	5·38	0·99	18·47
		3×P/3	525·7	5·12	0·75	14·63	550·3	5·36	0·55	10·24
		3×P	528·9	5·31	1·35	25·42				
		C	437·9	5·26	—	—	501·5	5·66	—	—
6	83	P	1302·0	4·99	0·89	17·95	1290·5	5·04	0·69	13·67
		3×P/3	1103·0	4·93	0·74	15·01	1279·7	5·25	0·40	7·68
		3×P	1393·0	5·15	1·32	25·60				
		C	896·2	5·10	—	—	1022·1	5·64	—	—

The red soil experiment was similar, except that the 3 × P treatment was omitted and only three rows each were available for the C and the 3 × P/3 treatments. Treatment plots were randomised in the usual manner.

The first application of fertilizer was made on the 28th October, 1952, and the plants were transplanted the following day. Harvesting was again carried out by taking five plants from each row 13, 27, 41, 55, 69 and 83 days after planting, and these samples are referred to as Series 1 to 6.

CHEMICAL AND RADIOMETRIC ANALYSIS

The procedure followed was similar to that adopted in previous experiments[1,2]. Controls were checked for activity due to potassium and certain results in series 6, where this activity amounted to more than 5 *per cent.*, were corrected to allow for this effect.

RESULTS

The mean dry weight yield per five plants at each harvest, together with results of the chemical and radiometric analysis for phosphate in the plant material, are set out in Table I. The percentage of fertilizer phosphate to total phosphate for each treatment and each growth stage is also shown. Following the table, a summary of the main significant differences is given.

In Table II the total phosphate uptake per five plants and fertilizer fraction at each growth stage are shown, together with the difference between these amounts, which gives a figure for soil phosphate absorption for each treatment. Significant differences are summarised below the table.

SUMMARY OF SIGNIFICANT DIFFERENCES TABLE I

		Black Soil	*Red Soil*
Series 1	Dry weight	N.S.D.	P>C
	Total P_2O_5	P>P/3>C	N.S.D.
	Fert. P_2O_5	P>P/3	N.S.D.
Series 2	Dry weight	P>C	N.S.D.
	Total P_2O_5	N.S.D.	N.S.D.
	Fert. P_2O_5	P>P/3	P>P/3
Series 3	Dry weight	2×P>C	P>C
	Total P_2O_5	N.S.D.	N.S.D.
	Fert. P_2O_5	P and 2×P>2×P/3	P>2×P/3
Series 4	Dry weight	2×P>C	N.S.D.
	Total P_2O_5	2×P>P	N.S.D.
	Fert. P_2O_5	P and 2×P>2×P/3	P>2×P/3
Series 5	Dry weight	3×P>C	N.S.D.
	Total P_2O_5	N.S.D.	N.S.D.
	Fert. P_2O_5	P and 3×P>3×P/3	P>3×P/3
Series 6	Dry weight	P and 3×P>C	N.S.D.
	Total P_2O_5	N.S.D.	N.S.D.
	Fert. P_2O_5	3×P>P>3×P/3	P>3×P/3

TABLE II

Series	Days after planting	Treatment	Black Soil			Red Soil		
			Total fert. P_2O_5 uptake mg.	Total P_2O_5 uptake mg.	Soil P_2O_5 mg.	Total fert. P_2O_5 uptake mg.	Total P_2O_5 uptake mg.	Soil P_2O_5 mg.
1	13	P	7·13	36·86	29·73	5·91	36·46	30·55
		P/3	3·13	31·78	28·65	2·36	27·42	25·06
		P	9·12	43·30	34·18			
		C	—	24·52	24·52	—	21·25	21·25
2	27	P	72·94	120·65	47·71	65·32	113·03	47·72
		P/3	22·01	69·23	47·22	30·45	96·38	65·93
		P	62·57	116·63	54·06			
		C	—	64·05	64·05	—	66·87	66·87
3	41	P	266·65	592·25	325·25	236·08	726·39	489·81
		2×P/3	99·37	477·84	378·47	101·70	613·39	511·68
		2×P	243·90	564·66	320·76			
		C	—	371·99	371·99	—	411·15	411·15
4	55	P	434·61	1334·09	899·48	436·29	1440·94	1004·65
		2×P/3	210·26	1147·33	937·07	213·27	1431·33	1218·06
		2×P	424·19	1285·63	861·44			
		C	—	924·37	924·37	—	1163·49	1163·49
5	69	P	762·27	3058·73	2296·46	573·92	3133·37	2559·45
		3×P/3	380·87	2684·21	2303·34	290·38	2964·93	2674·55
		3×P	711·28	2807·79	2096·51			
		C	—	2313·90	2313·90	—	2841·69	2841·69
6	83	P	1180·27	6541·28	5361·02	885·27	6487·37	5602·13
		3×P/3	790·63	5438·74	4648·11	468·98	6899·52	6403·54
		3×P	1829·64	7187·65	5358·00			
		C	—	4568·32	4568·32	—	5796·82	5796·82

SUMMARY OF SIGNIFICANT DIFFERENCES TABLE II

		Black Soil	*Red soil*
Series 1	Fert. P_2O_5	P>P/3	N.S.D.
	Total P_2O_5	P>C	P>P/3>C
	Soil P_2O_5	P>C	P>P/3>C
Series 2	Fert. P_2O_5	P>P/3	N.S.D.
	Total P_2O_5	P>C	N.S.D.
	Soil P_2O_5	N.S.D.	P>C
Series 3	Fert. P_2O_5	P and 2×P>2×P/3	P>2×P/3
	Total P_2O_5	2×P>C	P>C
	Soil P_2O_5	N.S.D.	N.S.D.
Series 4	Fert. P_2O_5	P and 2×P>2×P/3	P>2×P/3
	Total P_2O_5	2×P>C	N.S.D.
	Soil P_2O_5	N.S.D.	N.S.D.
Series 5	Fert. P_2O_5	P and 3×P>3×P/3	P>3×P/3
	Total P_2O_5	N.S.D.	N.S.D.
	Soil P_2O_5	N.S.D.	N.S.D.
Series 6	Fert. P_2O_5	3×P>P and 3×P/3	P>3×P/3
	Total P_2O_5	3×P and P>C	N.S.D.
	Soil P_2O_5	N.S.D.	N.S.D.

The approximate amount of phosphate that would be utilised per morgen of tobacco as calculated from analysis figures for series 6 is shown in Table III.

TABLE III

PHOSPHATE ABSORPTION PER MORGEN (POUNDS)

Treatment	*Black Soil*			*Red soil*		
	Fert.	Soil	Total	Fert.	Soil	Total
P	11	50	61	8	52	60
3×P/3	8	42	50	4	60	64
3×P	17	50	67	—	—	—
C	—	42	42	—	54	54

DISCUSSION OF RESULTS

From Table I it is clear that there was no significant difference in the growth of the tobacco as determined by dry weight between any of the various phosphates treatments on the black soil. The P and 3 × P treatments, however, gave significantly greater plant weight than the controls. The 3 × P/3 treatment also gave better growth than the controls, but the figures were not quite significant at the 0·05 level.

For the total P_2O_5 concentration in the plant, it is seen that, except in the very early growth stage, there was little significant difference between any of the treat-

ments. The fertilizer phosphate concentration in the plants is higher, especially in the early stages, for P and 3 × P treatments, as compared with the 3 × P/3 treatment, but the difference becomes progressively less with time. At the last harvest, the 3 × P treatment has produced a significantly higher fertilizer phosphate concentration than the P treatment. On the red soil similar results were obtained, although with the smaller number of replications, the growth differences were not quite significant, and no significant difference was apparent in the total P_2O_5 concentration in the plant material. For fertilizer phosphate, the P treatment gave significantly increased fertilizer concentration compared with the 3 × P/3 treatment, especially in the early growth stages.

The practical significance of these results is made clearer from Table II, in which total phosphate and total fertilizer phosphate uptake by the five plants sampled at each harvest is given. Here it is seen that on the black soil the P and 3 × P treatments have certainly resulted in a greater total phosphate uptake than the controls, whereas the 3 × P/3 treatment figures are not quite significantly higher than those from the untreated plots. For fertilizer phosphate the P and 3 × P treatments gave higher absorption figures than the 3 × P/3 treatment, and at the last harvest the 3 × P treatment gave figures significantly higher than the P treatment. On the red soil the P treatment gave a significantly higher fertilizer phosphate uptake than the 3 × P/3 treatment. On both soils the total phosphate uptake from soil reserves was not significantly different for any series, even including the control plots.

CONCLUSIONS

The treatments above refer to a 4N.12P.6K mixture, whereas in the previous study[2] the mixture used was 2N.12P.6K. Comparison with this previous work shows that the increase in nitrogen has not resulted in an increase in phosphate uptake.

From the practical point of view of tobacco cultivation on these soils it would appear, therefore, that the recommended dressing of 800 lb. per morgen of a 2N.12P.6K mixture, *i.e.*, 96 lb.P_2O_5 per morgen before planting is quite adequate for the phosphate nutrition of the tobacco. Split applications of one-third before planting followed by two further side dressings during growth have, if anything, given poorer growth. Trebling the amount applied has not improved growth, although there was a slightly higher phosphate concentration in the plant at the late growth stage. It is clearly evident, however, that, although the soil phosphate reserves are at a high level in these soils, presumably because of repeated phosphate applications in previous years, it is still essential to provide a source of readily available phosphate in the early growth stages. As the root system develops and a larger volume of soil is explored, the plants can apparently obtain adequate phosphate from soil phosphate reserves during the later growth stages. The picture may, of course, be entirely different where the soil phosphate reserves are at a lower level, even on the same soil types.

The percentage of total fertilizer phosphate applied that was taken up by the plants is as follows:-black soil, P treatment 11·8 *per cent.*, 3 × P/3, 7·9 *per cent.*, and 3 × P, 6·1 *per cent.* Red soil, P, 8·9 *per cent.*, and 3 × P/3, 4·7 *per cent.* On both soils, therefore, the most efficient use of the applied phosphate was obtained by the pre-planting application P.

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THE NITRIC ACID OXIDATION OF COAL—PART IV.

APPLICATION OF THE GRAPHICAL-STATISTICAL METHOD TO THE INTERPRETATION OF THE INVESTIGATIONS ON THE NITRO-HUMIC ACIDS

by

B. L. van DUUREN

OPSOMMING

'n Nuwe grafies-statistiese metode om reaksiemeganismes en -produkte voor te stel, soos deur Van Krevelen[1] ontwikkel, is gebruik om die reaksies van die nitrohumiensure, verkry uit die oksidasie van steenkool, te verklaar.

SUMMARY

A new graphical statistical method of representation of reaction mechanisms and products, developed by Van Krevelen[1], has been used in the interpretation of the reactions of the nitro-humic acids from coal oxidation.

In a recent publication Van Krevelen[1] developed a new graphical-statistical method for the study of problems connected with the structure and reaction processes of coal. In this method use is made of a diagram in which the hydrogen-carbon atomic ratio is plotted against the oxygen-carbon ratio. He showed that reactions such as oxidation, dehydrogenation, hydrogenation, dehydration, demethanation and decarboxylation are represented by straight lines. He proved mathematically that in the diagram decarboxylation is represented by a straight line which connects the composition of the starting material (C/H, C/O ratios) with the point C/H = 0, C/O = 2. Similarly dehydration is represented by straight lines which have a slope equal to 2. Oxidation and deoxygenation are indicated by horizontal straight lines, while hydrogenation and dehydrogenation are represented by vertical straight lines.

This method has now been applied to the products from various reactions on the mixture of ether-insoluble nitrohumic acids obtained from the nitric acid oxidation of coal as was described in Part II[2] of this series, as well as to the products from fraction I, which was prepared by a method employing fractional precipitation of an acetone solution of the mixture with ether. The method has been found to be a useful indication of the nature of the reactions.

REACTIONS

The method was applied to the results of the investigations on the mixture of acids as well as to those on fraction I, since the results of the former are related to those of the latter.

(i) **Reactions on the humic acid mixture.** Various reactions on the ether-insoluble mixture of nitro-humic acids were described in PartII[2] and are again given briefly below. The H/C and O/C ratios of the reaction products were calculated and plotted on a H/C : O/C diagram shown in Figure 1. The reactions, the percentage composition of the products, the atomic ratios and the number of the product are summarised in Table I.

(a) *Alkali-treatment:* The ether-insoluble product obtained directly from the oxidation was found to be only partially soluble in acetone and alcohol. However, if the product was dissolved in alkali and the alkaline solution acidified immediately, a product was obtained which was completely soluble in both solvents but still insoluble in ether. In Part II[2] it was suggested that this change was probably due to the hydrolysis of either anhydrides or lactones or both. From the slope of the line joining 1 (original product) to 2 (alkali-treated product) in Figure 1 it may be deduced that the alkali-treatment involves a hydration reaction.

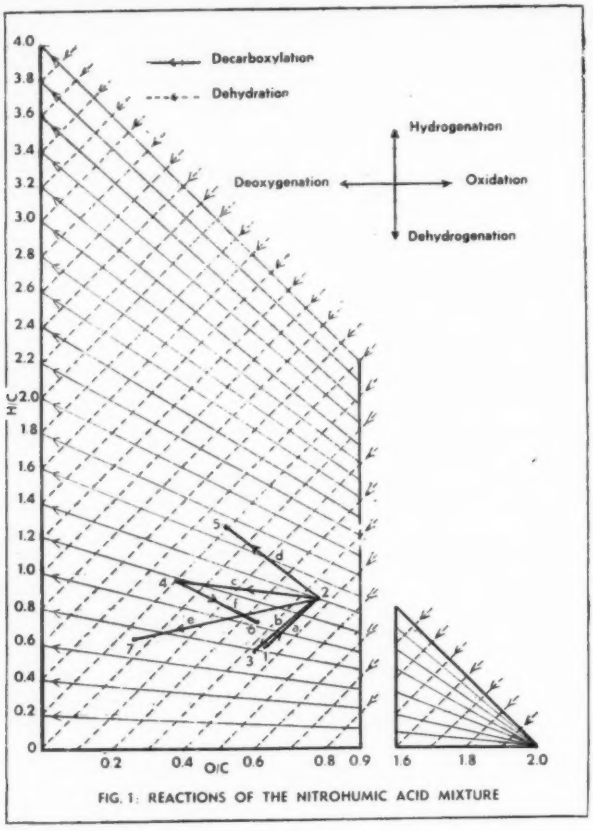

FIG. 1: REACTIONS OF THE NITROHUMIC ACID MIXTURE

(b) Prolonged treatment of the alkali-treated ether insoluble mixture with concentrated nitric acid yielded ether-insoluble products of almost constant composition (Table I No. 3). From Figure 1 it is clear that this reaction involves the opposite of (a) *i.e.* a dehydration reaction.

(c) *and* (d) The mixture of alkali-treated ether-insoluble acids on reduction with zinc dust and hydrochloric acid yielded a product which was separated chromatographically into two fractions. (Table I, numbers 4 and 5). From Figure 1 it may be deduced that the hydrogenation is accompanied by deoxygenation.

(e) *Decarboxylation:* The alkali-treated ether-insoluble product was decarboxylated in a heated suspension of copper powder in quinoline. Product 7, Table I, was obtained and it was found that carbon dioxide was evolved during the reaction. The reaction (e), Figure 1, which represents this reaction is interesting. The direction of the line is not what one would normally expect from a loss of carbon dioxide only. It appears that in the decarboxylation both carbon dioxide and water are eliminated as had previously been deduced from a study of the analytical results as such (see Part II *loc. cit.*).

(f) *Oxidation of the reduced product:* Reaction (f) Figure 1 which represents the nitric acid oxidation of the reduced product, indicates that the oxidation is accompanied by a dehydrogenation reaction.

TABLE I

ATOMIC RATIOS OF REACTION PRODUCTS OF THE NITROHUMIC ACID MIXTURE

Origin of Product	*Percentages* C	H	N	*Atomic Ratios* H/C	O/C	*Number*
Ether-insoluble product direct from oxidation	50·76	2·48	3·78	0·58	0·63	1
Ether-insoluble product after alkali-treatment	45·79	3·24	3·80	0·85	0·78	2
Alkali-treated product treated with nitric acid for 27 hours and subsequently treated with alkali	51·41	2·36	4·77	0·55	0·60	3
Zinc-hydrochloric acid reduction product of alkali-treated mixture separated chromatographically. Fraction I	60·82	4·89	2·82	0·96	0·38	4
do. Fraction II	54·67	5·73	1·38	1·26	0·52	5
HNO_2-oxidation product of 4	51·19	3·09	4·09	0·72	0·61	6
Decarboxylation product of alkali-treated product	65·95	3·44	7·50	0·63	0·26	7

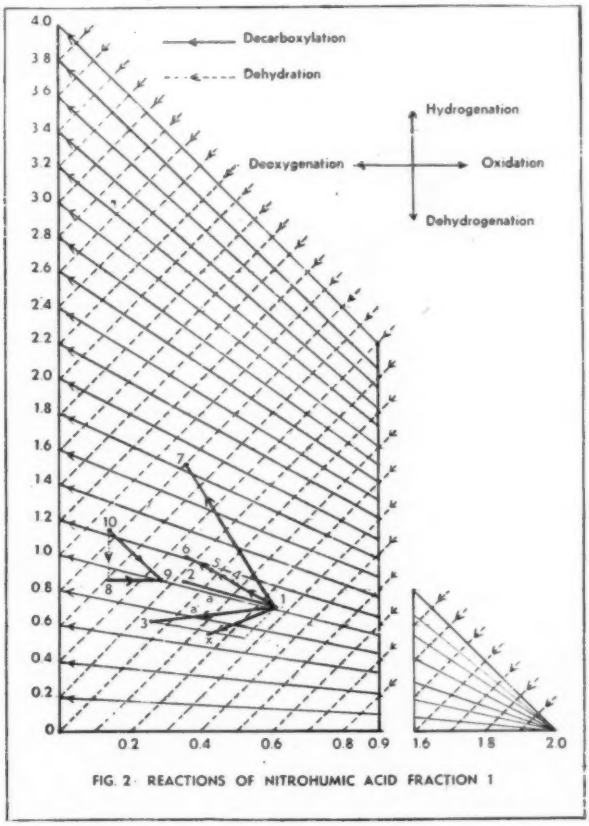

FIG. 2. REACTIONS OF NITROHUMIC ACID FRACTION 1

(ii) **Reactions of nitrohumic acid fraction I.** Nitrohumic acid fraction I was obtained from the mixture of the ether-insoluble acids by precipitation of an acetone solution of the mixture with ether (Part III). Various reactions were carried out on this fraction and the H/C and O/C ratios of the products are plotted on the diagram in Figure 2.

(a) *Decarboxylation:* The nitrohumic acid fraction I (1, Table II) was decarboxylated with copper powder in the presence of quinoline and phenol. A fraction of the product was found to be soluble in methyl ethyl ketone (2, Table II) while the residue (3, Table II) was found to be insoluble in this solvent.

The decarboxylation reaction is represented in Figure 2 by lines a and a′. The reaction by which product 2 is formed approaches a pure decarboxylation reaction. The reaction product is soluble in organic solvents such as methyl ethyl ketone. The reaction by which product 3 is formed (reaction line a′) appears to involve both decarboxylation and dehydration and is similar to that obtained from the mixture of humic acids (see Figure 1). This product is insoluble in most organic solvents but is soluble in pyridine. It was stated in Part II that the decarboxylation reaction on the mixture of nitrohumic acids appears to be accompanied by a condensation reaction in which water is lost. This view is further substantiated by the fact that in the presence of phenol, this condensation reaction appears to be at least partially, inhibited.

To clarify the above deductions it may be mentioned that an empirical formula of $C_{60}H_{40}N_4O_{38}$ was calculated for fraction I [2]. For the simultaneous loss of water and carbon dioxide *e.g.* 5 molecules of each, a product represented by x (H/C = 0·55, O/C = 0·42) in Figure 2 is obtained.

(b) *Reduction:* Fraction I was reduced with titanous chloride and hydrochloric acid to give product 4 of Table II. As in the case of the mixture of acids the hydrogenation is accompanied by deoxygenation which would be normally expected from the reduction of nitro groups, etc.

(c) *High-pressure hydrogenation:* Fraction I was subjected to high-pressure hydrogenation in the presence of Raney-nickel catalyst. Three products were obtained viz. a product soluble in methyl ethyl ketone, a product insoluble in methyl ethyl ketone and a viscous oil. These products are presented as 5, 6 and 7 in Table II and in Figure 2.

Like the titanous chloride reduction the high pressure hydrogenation appears to consist of both hydrogenation and deoxygenation. The titanous chloride reduction product, 4, and the high-pressure hydrogenation products, 5 and 6, fall on one line, appearing to indicate progressive hydrogenation and deoxygenation by one type of reaction. The liquid product 7, appears to be a product of hydrogenation of product 6.

TABLE II

ATOMIC RATIOS OF REACTION PRODUCTS OF NITROHUMIC ACID FRACTION I

Origin of Product	*Percentages*			*Atomic Ratios*		*Number*
Nitrohumic acid fraction I	50·86	2·99	4·13	0·70	0·61	1
Decarboxylation product I	63·13	4·47	2·66	0·85	0·35	2
Decarboxylation product II (Methyl ethyl ketone-insoluble)	67·54	3·52	4·21	0·62	0·26	3
Titanous chloride reduction product ..	57·35	4·08	1·23	0·85	0·48	4
High-pressure hydrogenation product (Methyl ethyl ketonesoluble)	62·38	5·16	2·42	0·91	0·43	5
High-pressure hydrogenation product (Methyl ethyl ketone-insoluble) ..	58·92	4·48	2·96	0·99	0·36	6
High-pressure hydrogenation product (liquid)	61·15	7·77	1·00	1·51	0·36	7

REMARKS

Van Krevelen applied the graphical-statistical method for the determination of the structure and the reaction processes of coal. He illustrated this method for reactions of acetone and benzoic acid. It is found, for example, that the line joining the points representing benzaldehyde (Figure 2, 8, H/C = 0·86, O/C = 0·14) and benzoic acid (Figure 2, 9, H/C = 0·86, O/C = 0·29) has the direction of the lines representing oxidation. The line joining benzyl alcohol (Figure 2, 10, H/C = 1·14, O/C = 0·14) to benzoic acid, however, does not correspond with any of the lines representing the different reactions. If it is therefore known that the product (benzyl alcohol) has been oxidised and one assumes that oxidation has actually taken place to yield the oxidised product (benzoic acid), it may be deduced that the oxidation process has been accompanied by a dehydrogenation process viz. benzylalcohol to benzaldehyde (see dotted line between points 8 and 10).

The conclusions drawn from Figures 1 and 2 in connection with the reaction processes of humic acids have been based on the way of reasoning explained above. When, however, the H/C and O/C ratios of a number of related products are plotted on a diagram, without knowing the types of reactions that are involved in their production, it is practically impossible to deduce what relation the one bears to the others since any number of different reaction lines may be followed from one point to another.

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CALIBRATION OF A STORMER VISCOSIMETER WITH SPECIAL REFERENCE TO TURBULENT FLOW CONDITIONS.

by

P. J. VAN DER WALT and A. M. FOURIE

OPSOMMING

Bekende metodes vir die kalibrering van die Stormer-viskosimeter is nagegaan, en daar is vasgestel dat hulle nie onder alle omstandighede geldig is nie. Die enigste algemene vergelyking wat van toepassing skyn te wees op die instrument kan egter nie in 'n bruikbare matematiese vorm uitgedruk word nie, behalwe in gevalle waar die veranderlikes binne sekere enge perke lê. Betroubare resultate word egter verkry deur gebruik te maak van kalibreringskurwes wat die verhouding tussen die weerstandskoëffisiënt en die Reynoldsgetal onder die besondere toetsomstandighede aandui.

SUMMARY

Known methods of calibrating a Stormer Viscosimeter were studied and it was found that these were not valid under all conditions. The only general equation which appears to be applicable to the instrument is not expressible in usable mathematical form, except for narrow ranges of variables. Reliable results are best obtained by making use of calibration curves showing the relationship of a coefficient of resistance to the Reynolds' number for particular test conditions.

INTRODUCTION

In the course of studies of the characteristics of suspensions of finely ground solids in water, it was decided to use a Stormer Viscosimeter[1] for determining the apparent viscosity of the suspensions.

The range of viscosities that were of interest in this investigation was rather lower than that for which the instrument is normally used. This has necessitated a more detailed study of the characteristics of the instrument. Some results of general interest are described in this paper.

THE STORMER VISCOSIMETER

The operating principle of the Stormer Viscosimeter is illustrated diagrammatically in Figure 1.

A rotor of suitable form is immersed in the liquid, whose viscosity is to be determined and is rotated by means of a driving weight through a set of gears as indicated. Determinations are made only while the rotor is running at constant speed. At the commencement of any experiment the driving weight is therefore permitted to fall until the rotor has attained a constant speed. Thereafter, the time required for the rotor to make a fixed number of revolutions is determined. This procedure is repeated using a number of driving weights and the viscosity of the test liquid is determined from the calibration data relating to the instrument in the manner to be described.

CALIBRATION OF STORMER VISCOSIMETER

There are two general methods in use for obtaining usable results with the Stormer Viscosimeter. In the first method the "Relative Viscosity" is determined. This is obtained by dividing the time required for the rotor to make, say, 100 revolutions in the test liquid by the time required to make 100 revolutions in distilled water (or some other standard liquid) using the identical procedure, temperature and driving weight in both cases. In the second method the instrument is calibrated in terms of absolute viscosity units (poises) using liquids of known viscosities. The present paper is confined to a discussion of the latter method.

A series of tests was carried out on liquids of known viscosity and density using the cylindrical rotor shown in Figure 2. The results of these tests, together with other relevant data are reported in Table I.

OPERATING PRINCIPLE OF THE STORMER VISCOSIMETER

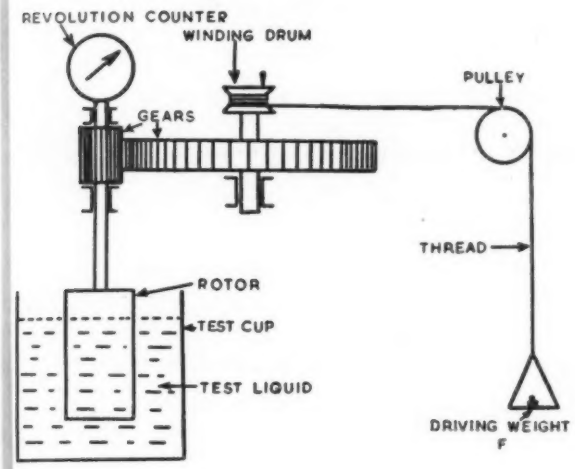


FIGURE 1.

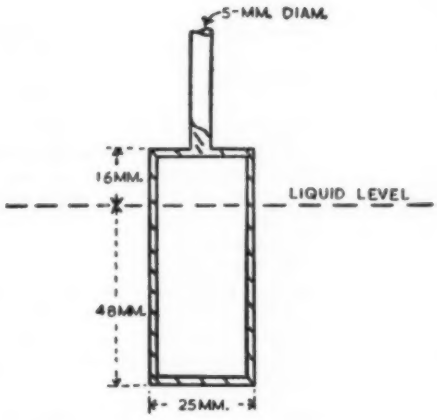
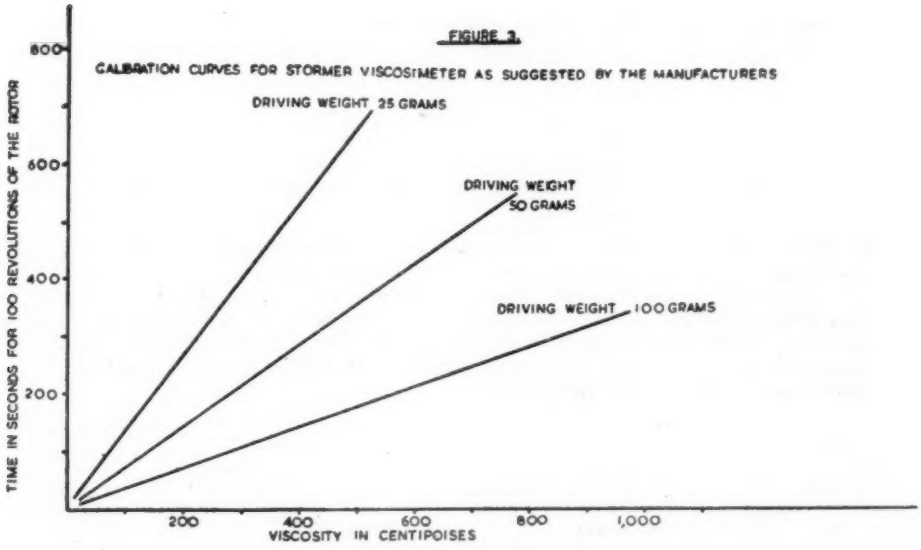


FIGURE 2. HOLLOW CYLINDRICAL ROTOR.

FIGURE 3.



The frictional resistance of the instrument was found to be of the order of 1 to 2 grams. When large driving weights are used this may be negligible, but in these experiments where only small driving weights were used a correction was desirable. Accordingly, the effective driving weights reported in Table I were obtained by subtracting the average weight required just to set the instrument in motion in air from the total driving weight used for each test.

The liquids were maintained at $30 \pm \frac{1}{2}$°C. by using a suitable water jacketed container.

The methods of calibrating the instrument are conveniently discussed with reference to the data in Table I.

Method proposed by manufacturers of the Stormer Viscosimeter. The manufacturers of the instrument[2] suggest that it can be calibrated by plotting the time, in seconds, required for 100 revolutions of the rotor against the viscosity of liquids of known viscosity, holding the driving weight and temperature constant. In this way, it is stated, a family of calibration curves can be prepared for various driving weights as shown in Figure 3. It will be observed that it is apparently taken for granted that a linear relationship exists between the time taken for 100 revolutions and the viscosity for each driving weight. If such a procedure were valid it would be a most convenient method for calibrating the instrument and for determining the viscosity of an unknown liquid in terms of absolute units. It may be noted that the density of the liquid is not taken into account in this method.

Such a family of curves was plotted as shown in Figure 4 from the data in Table 1. A number of the values plotted in Figure 4 were obtained by interpolation from the data in Table I, but a mass of other test data indicate that this will not affect the general picture.

It will be observed in Figure 4 that the test results do not fall particularly well on the so-called calibration straight lines. It is not possible either to draw any other form of curve with any confidence. In view of the care with which the test work had been carried out, it was considered that this scatter of the points could not be entirely ascribed to experimental error. It was concluded therefore, that the procedure described was not valid under all conditions and that its use was liable to lead to serious error in some instances.

Method proposed by Geddes and Dawson. Geddes and Dawson[3] and others state that the general viscosity equation for instruments of the Stormer type is given by:

$$\eta = Ft/A \qquad (1)$$

where η = viscosity of the liquid (poises),
F = driving weight,
t = time for a fixed number of revolutions of rotor,
and A = a constant for the particular instrument, rotor, and test conditions, etc.

In other words, if equation (1) were valid over the whole range of variables studied, one would expect the speed of the rotor to be proportional to the driving weight.

Geddes and Dawson carried out tests on a number of oils ranging in viscosity from 6·03 to 33·7 poises. With the exception of the most viscous oil, these tests did not show a linear relationship between the speed of the rotor and the driving weight. They concluded that a kinetic energy correction should be applied to equation (1), which was accordingly modified to read:

$$\eta = \frac{Ft}{A} - \frac{C\rho}{t} \qquad (2)$$

where ρ = density of the liquid
and C = a constant.

TABLE I

RESULTS OBTAINED USING A CYLINDRICAL ROTOR

Liquid	Viscosity* at 30°C (cS.)	Density (ρ) at 30°C. (g. cm.$^{-3}$)	Viscosity at 30°C. (cP.)	Effective Driving Weight (F). (g.)	Time for 100 Revs. (t). (sec.)	Re/B	ρ/t^2	QB^2
Solution of Glycerine in water	85·55	1·230	105·2	16·3	43·63	0·0268	0·000645	25,270
				18·3	39·18	0·0298	0·000800	22,875
				21·3	34·09	0·0342	0·001056	20,170
				24·3	30·38	0·0385	0·001331	18,260
				28·3	26·82	0·0436	0·001711	16,540
				33·3	23·74	0·0492	0·002180	15,270
				38·3	21·37	0·0547	0·002694	14,220
				38·3	21·37	0·0547	0·002694	14,220
Solution of Glycerine in water	31·28	1·201	37·57	7·3	45·23	0·0706	0·000587	12,440
				8·3	41·33	0·0774	0·000703	11,810
				10·3	35·13	0·0911	0·000976	10,550
				12·3	30·90	0·1036	0·001261	9,750
				14·3	27·49	0·1164	0·001591	8,990
				16·3	24·90	0·1285	0·001941	8,400
				18·3	22·83	0·1400	0·002304	7,940
				20·3	21·03	0·1522	0·002721	7,460
				22·3	19·50	0·1640	0·003161	7,050
				26·3	17·15	0·1864	0·004082	6,440
				31·3	15·1	0·2116	0·005263	5,950
Zinc-chloride Solution ..	11·01	1·908	21·01	5·3	50·0	0·1817	0·000763	6,950
				6·3	43·4	0·209	0·001013	6,220
				8·3	34·9	0·260	0·001566	5,300
				10·3	29·9	0·304	0·002133	4,830
				12·3	26·5	0·343	0·002717	4,530
				15·3	22·8	0·398	0·003669	4,170
				18·3	20·1	0·452	0·004722	3,875
Calciumchloride solution.. ..	10·44	1·464	15·28	4·3	43·9	0·218	0·000761	5,650
				5·3	37·6	0·255	0·001036	5,120
				6·3	33·2	0·288	0·001326	4,750
				7·3	30·1	0·318	0·001614	4,520
				8·3	27·7	0·346	0·001908	4,350
				9·3	25·6	0·375	0·002238	4,155
				11·3	22·5	0·425	0·002886	3,915
				13·3	20·2	0·474	0·003587	3,710
				15·3	18·45	0·519	0·004301	3,560
Pentachloroethane oil ..	6·785	1·312	8·90	4·3	32·95	0·447	0·001204	3,570
				5·3	28·75	0·513	0·001589	3,340
				6·3	25·94	0·569	0·001955	3,220
				7·3	23·91	0·616	0·002292	3,180
				8·3	22·48	0·656	0·002598	3,190
				10·3	19·73	0·747	0·003372	3,050
Solution of Glycerine in water	5·44	1·142	6·21	2·3	38·60	0·476	0·000766	3,000
				3·3	32·41	0·568	0·001090	3,030
				4·3	28·01	0·656	0·001455	2,960
				5·3	24·77	0·743	0·001864	2,840
				6·3	22·60	0·813	0·002231	2,825
				7·3	20·85	0·882	0·002631	2,770
Oil	38·475	·873	33·59	7·3	37·4	0·0694	0·000622	11,730
				9·3	31·6	0·0821	0·000872	10,670
				11·3	27·43	0·0949	0·001163	9,720
				13·3	24·53	0·1060	0·001453	9,150
				15·3	22·1	0·1175	0·001783	8,580
				17·3	20·3	0·1281	0·002121	8,160

*Determined in an Ubbelohde viscosimeter

This equation can be further rearranged to the form

$$\eta = t(F—K'\rho/t^2)/A \qquad (3)$$

where $K' = CA$.

Geddes and Dawson were then able to find values for the constants K′ and A from their experimental data which made equation (3) valid within approximately 5 per cent. over the range of variables covered during their study.

This procedure was applied to the data in Table I and values for the constants K′ and A were calculated for each of the liquids. Mean values of these constants are tabulated in Table II.

TABLE II

Mean Values of K′ and A Calculated from the data in Table I.

Viscosity, cP.	K′	A
6.21	2,400	306
15·28	2,050	785
21·00	1,940	881
33·59	3,550	586
37·57	2,930	692
105·23	3,090	590
Mean	2,660	640

It will be observed in Table II that the values of the constants K′ and A vary considerably from liquid to liquid. The latter constant which is the more important one in equation (3) is particularly variable. Clearly, a general equation using mean values of K′ and A would not fit the facts very well and could lead to serious errors.

It was again considered that the variations in the values of the so-called constants K′ and A could not be entirely ascribed to experimental error and it was concluded that equation (3) is not generally valid for a Stormer Viscosimeter. In addition in the light of later knowledge, it is doubtful whether this equation can be regarded as being more than an empirical approximation even in the range of variables studied by Geddes and Dawson. A careful study of their test data showed that the value of A was reasonably steady from liquid to liquid (within about 5 per cent.) but the value of K′ varied considerably (from about 11,000 for one oil to 32,500 for another). Such a variation in K′ does not support their theory particularly well.

Authors' proposed method. In view of the fact that the usual methods of calibrating the Stormer Viscosimeter in terms of absolute units did not appear to be valid in the range of variables under consideration, it was necessary to study the subject with a view to evolving a more acceptable procedure. The method to be described was finally considered the most suitable and the one having the most scientific justification.

In principle, the Stormer Viscosimeter provides a means of measuring the resistance experienced by an object when moving (or rotating) in a viscous fluid. Now it is well known [4] that under certain conditions the motion of a fluid becomes exceedingly complex and is beyond existing methods of calculation. It may well be that such conditions prevail in some instances when using the Stormer Viscosimeter, so that it may be impractical to establish an equation relating the resistance experienced by the rotor to its speed, the viscosity of the liquids, etc.

Several workers have found that the most practical procedure when studying the motion of a body in a fluid is to modify an equation based on the normal scientific principles by means of a suitable coefficient. This coefficient has been found to be a

somewhat complex function of the Reynolds' Number. Curves relating the coefficient of resistance of spheres [5] and other bodies of regular shape to their Reynolds' Number (**Re**) are well known and appear in several technical publications. In the case of a sphere, for example, the coefficient of resistance is inversely proportional to $\mathbf{Re}^n$ and n varies from about 0 to 1. At very low values of the Reynolds' Number, the coefficient of resistance is inversely proportional to **Re** and at very high values the coefficient of resistance is approximately constant. Low values of **Re** represent laminar flow, while high values represent turbulent flow conditions.

The use of a coefficient of resistance appeared a most promising method of calibrating the viscosimeter and this was investigated.

The Reynolds' Number of an object in motion in a fluid is given by the equation [4]

$$\mathbf{Re} = L\rho V/\eta \qquad (4)$$

where L = a characteristic linear dimension of the object,
ρ = density of the fluid,
V = velocity of the object,
and η = viscosity of the fluid (poises).

In the case of the rotor of the Storm Viscosimeter, the characteristic length is a constant for a given rotor and its value is of no real interest. Similarly, the velocity of the rotor is inversely proportional to the time, t, required to make a fixed number of revolutions. Hence equation (4) may be modified to read:

$$\mathbf{Re} = B\rho/\eta t \qquad (5)$$

where B is a constant.
Clearly, the value of the constant B changes if the dimensions or form of the rotor are changed.

The present authors were principally interested in a viscosity range between the limits of about 1 to 100 cP. and intended using relatively high rotor speeds. Low viscosity and high velocity implied relatively high values of the Reynolds' Number which in turn suggested that the tests would be carried out under turbulent or near turbulent conditions of flow.

The resistance experienced by a body is given by the general equation [4]

$$F = QL^2\rho V^2 \qquad (6)$$

where F = resistance = driving weight in the case of the Stormer Viscosimeter,
Q = resistance coefficient,
L = linear dimension as before (constant for a given rotor),
ρ = density of fluid,
and V = velocity of the body (proportional to 1/t).

Rearranging equation (6) it can be shown that

$$Q = Ft^2/B^2\rho. \qquad (7)$$

The values of **Re** and Q were calculated from the test data in Table I, using equations (5) and (7) respectively and Q was plotted against **Re** in Figure 5.

It will be observed in Figure 5 that a definite relationship appears to exist between the coefficient of resistance and the Reynolds' Number in the case of the cylindrical rotor used (Figure 2), notwithstanding relatively large variations in the density and viscosity of the test liquids. Within the range of variables investigated and using the cylindrical rotor described, Q is proportional to $\mathbf{Re}^{-0.65}$.

If log Q is plotted against log **Re** for each liquid, it will be noted that all the points for all the liquids do not fall smoothly on the curve, particularly in the tests where the driving weights were small. This is probably due to experimental error and the fact that the frictional resistance of the instrument is relatively high compared with the driving weights. It was found during the experimental work that the frictional resistance varied, possibly due to variation in ambient temperature, etc. The correction applied was an average value of the driving weight required just to set the

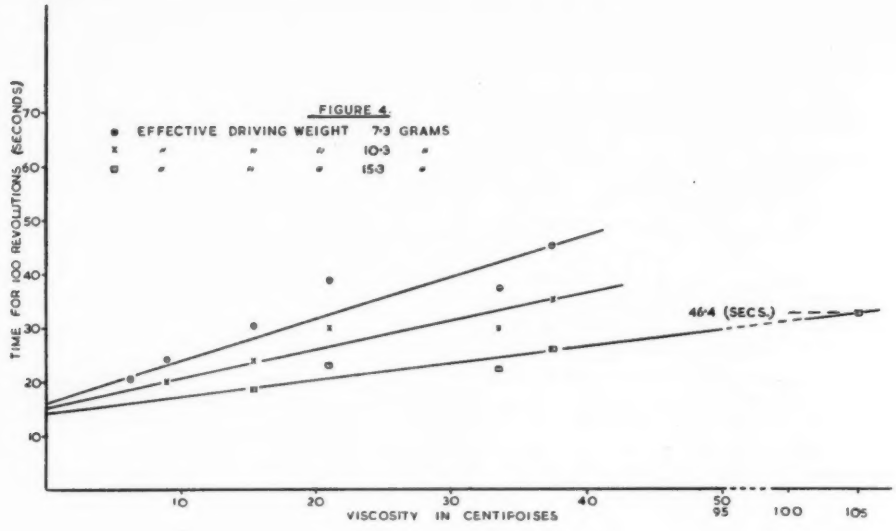


FIGURE 4.
EFFECTIVE DRIVING WEIGHT 7·3 GRAMS
" " " " 10·3 "
" " " " 15·3 "
TIME FOR 100 REVOLUTIONS (SECONDS)
VISCOSITY IN CENTIPOISES
46·4 (SECS.)

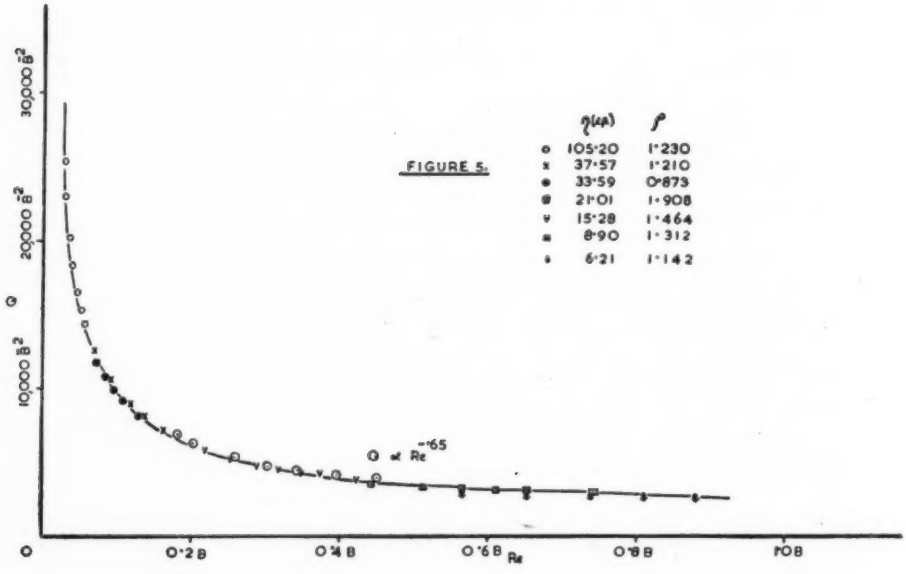


FIGURE 5.
η(cp) ρ
105·20 1·230
37·57 1·210
33·59 0·873
21·01 1·908
15·28 1·464
8·90 1·312
6·21 1·142
Q
Q ∝ Re^-1·65
Re

instrument in motion and since the frictional resistance probably varies with the speed of the rotor, it will be clear that the values of the effective driving weights reported are only approximations.

It is accordingly considered that only the general relationship found between Q **Re** is of significance. In order to establish the limitations of the procedure described and a more sensitive instrument and carefully controlled test conditions will be required.

A further series of tests was carried out using a rotor of the form shown in Figure 6. Results of these tests together with calculated values of Q and **Re** are reported in Table III. Values of Q are plotted against **Re** in Figure 7.

It will be observed that a definite relationship again appears to exist between Q and **Re** despite the radical change in the form of the rotor. In this case, however, Q is approximately proportional to $\mathbf{Re}^{-0\cdot19}$. Since liquids of the same order of viscosity and density were used as in the previous series of tests, it is clear that the form of the rotor has an important influence on the relationship between Q and **Re**.

Values of Q and **Re** were calculated from the test data reported by Geddes and Dawson[3] with the results shown in Table IV. The corresponding plot of Q versus **Re** is shown in Figure 8. Geddes and Dawson used a submerged paddle type rotor as indicated in Figure 9.

Geddes and Dawson's data also supported the theory that a definite relationship exists between the coefficient of resistance and the Reynolds' Number for the Stormer Viscosimeter and that this fact can be used to calibrate the instrument. Under their test conditions (viz. viscosities in the range 6 — 33 P., etc.), Q is approximately proportional to $\mathbf{Re}^{-0\cdot92}$.

Suppose Q were proportional to $\mathbf{Re}^{-1}$ so that $Q = k.\mathbf{Re}^{-1}$, under certain conditions (viz. laminar flow), then from equations (5) and (7) it follows that

$$F = \frac{B^2\rho}{t^2}.k.\frac{\eta t}{B\rho} = Bk\eta/t, \qquad (8)$$

$$\text{whence } \eta = Ft/Bk \qquad (9)$$

This is the equation stated by Geddes and Dawson to be the general viscosity equation for instruments of the Stormer type (see equation 1). Their test conditions were very close to this (i.e. $Q \propto \mathbf{Re}^{-0\cdot92}$) particularly in the case of the highest viscosity oil which approximates closely to $Q \propto \mathbf{Re}^{-1}$, hence a slight modification to the equation (viz. "kinetic energy" correction) was a reasonable empirical approximation. In the case of very low viscosities (1 to 100 cP., say) equation (1) is entirely invalid, and it cannot, therefore, be regarded as the general equation for the instrument. Equation (6) appears to be the only general equation which applies. Unfortunately Q cannot be defined mathematically except for a rather narrow range of variables at a time

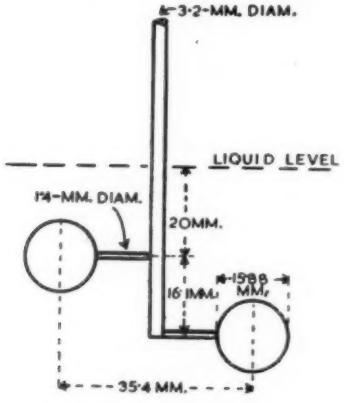
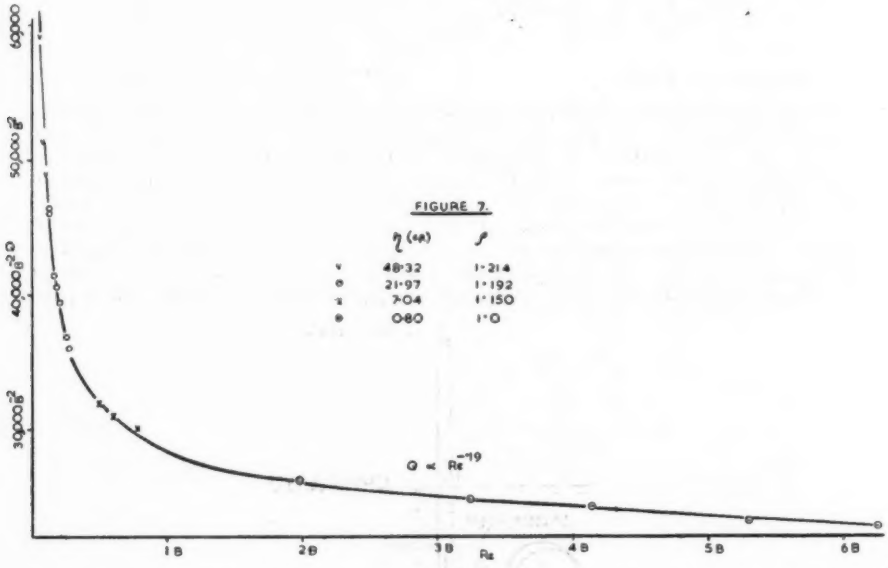


FIGURE 6. ROTOR CONSISTING OF 2 SPHERES

TABLE III

RESULTS OBTAINED USING A ROTOR CONSISTING OF TWO SPHERES AS IN FIG. 6

Liquid	Viscosity at 30°C. (cS.)	Density (ρ) at 30°C. (g. cm.$^{-3}$)	Viscosity at 30°C. (cP.)	Effective Driving Weight (F). (g.)	Time for 100 Revs. (t). (sec.)	Re/B	ρ/t^2	QB^2
Water	0·80	1·00	0·80	6·5	63·5	1·96	0·000248	26,210
				16·5	38·8	3·23	0·000664	24,850
				26·5	30·3	4·13	0·001089	24,330
				46·5	22·3	5·60	0·002010	23,130
				56·5	20·05	6·24	0·002488	22,710
Solution of Glycerine in water	6·125	1·150	7·04	16·5	50·7	0·322	0·000447	36,910
				31·5	34·15	0·478	0·000986	31,950
				46·5	27·7	0·589	0·001498	31,040
				76·5	21·3	0·766	0·002534	30,190
Solution of Glycerine in water	18·435	1·192	21·97	26·5	45·7	0·1188	0·000571	46,410
				36·5	36·8	0·1475	0·000880	41,480
				46·5	32·3	0·1682	0·001143	40,680
				56·5	28·9	0·1877	0·001427	39,590
				76·5	24·0	0·2262	0·002071	36,940
				96·5	21·1	0·2571	0·002677	36,050
Solution of Glycerine in water	39·8	1·214	48·32	26·5	52·15	0·0482	0·000447	59,280
				46·5	36·7	0·0683	0·000902	51,550
				76·5	27·9	0·0899	0·001560	49,040
				116·5	21·9	0·1148	0·002531	46,030



When the curve relating the coefficient of resistance to the Reynolds' Number has been established in the manner described, for a particular rotor and under fixed test conditions, the viscosity of an unknown liquid may be determined readily provided that its density is known. It is necessary merely to determine the speed of the rotor when a known driving force is applied. The coefficient of resistance, Q, may then be calculated from equation (7) and the corresponding value of the Reynolds' Number may be read from the calibration curve. The viscosity of the liquid is then calculated from equation (5). If desired, this procedure may be repeated for a number of other rotor speeds as a check.

TABLE IV

RESULTS OBTAINED BY GEDDES AND DAWSON

Liquid	Viscosity at 30°C. (cS.)	Density (ρ) at 30°C. (g. cm.$^{-3}$)	Viscosity at 30°C. (cP.)	Driving Weight (F). (g.)	Time for 100 Revs. (t). (sec.)	**Re**/B	ρ/t^2	QB^2
				50	83·3	0·001725	0·0001248	400,640
				100	43·2	0·00334	0·0004666	214,310
Oil	695·5	0·867	603	150	30·7	0·00469	0·0009216	162,760
				200	24·5	0·00587	0·001443	138,600
				250	20·2	0·00712	0·002124	117,700
				50	115·0	0·00102	0·0000721	693,580
				100	55·9	0·00211	0·0003073	325,410
Oil	848·8	0·959	814	150	39·2	0·00300	0·0006236	240,530
				200	30·3	0·00389	0·001044	191,570
				250	24·9	0·00474	0·001550	161,290
				300	21·4	0·00550	0·002092	143,400
				50	117·7	0·000824	0·0000636	786,410
				100	53·3	0·00166	0·0002573	388,650
Oil	1031·8	0·880	908	150	39·6	0·00244	0·0005588	268,430
				200	30·9	0·00314	0·0009238	216,490
				250	25·9	0·00374	0·001311	190,690
				300	22·0	0·00440	0·001814	165,380
				50	139·7	0·000590	0·0000447	1,118,560
				100	69·4	0·00119	0·0001818	553,090
				150	46·2	0·00178	0·0004069	368,640
Oil	1214·4	0·872	1059	200	35·3	0·00233	0·0006984	286,360
				250	28·4	0·00290	0·001080	231,390
				300	24·6	0·00335	0·001444	207,700
				350	21·7	0·00380	0·001853	188,880
				100	203·8	0·000134	0·0000221	4,522,800
				200	100·1	0·000272	0·0000915	2,185,300
Oil	367·5	0·917	3370	300	68·7	0·000397	0·0001955	1,534,500
				400	50·6	0·000539	0·0003595	1,112,700
				500	40·2	0·000678	0·0005685	879,500
				600	34·1	0·000797	0·0007872	762,100
				700	29·3	0·000928	0·001066	656,700
				800	25·8	0·001056	0·001380	579,700
				900	22·9	0·001189	0·001751	514,000
				1000	21·0	0·001295	0·002078	481,200

The objection may be raised that under certain test conditions there is no guarantee that an unknown liquid will fall precisely on the calibration curve and that an error may thus be made in determining the viscosity; if, for example, the instrument were calibrated in the near turbulent region and an unknown liquid were tested which actually falls in the streamline region. It is not considered, however, that such an error can be made since the calculated value of Q for the unknown liquid would in such circumstances fall outside the calibration curve.

To illustrate this point, the tests using the cylindrical rotor (Table I) were limited to the ranges 2,000 B^{-2} to 25,000 B^{-2} for Q, and 0·02B to 0·9B for **Re**. Since Q is approximately proportional to $\mathbf{Re}^{-0.65}$ it follows that the test conditions were carried out in the near-turbulent region.

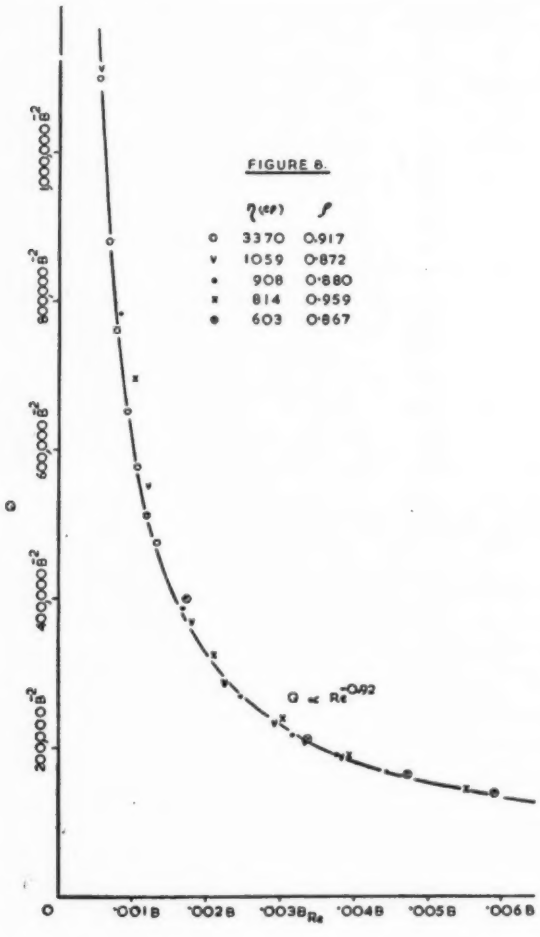
Castor oil having a viscosity of about 500 cP. was selected and a test was conducted with the results in Table V. In view of the high viscosity it was anticipated that the test would be carried out under streamline flow conditions, which should thus fall outside the calibration curve.

As will be seen from Table V, the ranges 70,000 B^{-2} to 500,000 B^{-2} for Q and ·01B to ·001B for **Re** fall outside the calibration curve; thus no mistake could be made. Clearly the calibration range would have to be extended if the viscosity of such a fluid is to be determined.

TABLE V

DETERMINATION OF THE VISCOSITY OF CASTOR OIL USING A CYLINDRICAL ROTOR

Liquid	Viscosity at 30°C (cS.)	Density (ρ) at 30°C. (g. cm.$^{-3}$)	Viscosity at 30°C. (cP.)	Effective Driving Weight (F). (g.)	Time for 100 Revs. (t). (sec.)	Re/B	ρ/t^2	QB^2
				22	148·6	0·001315	0·0000429	512,800
				32	103·4	0·001889	0·0000886	361,200
				42	79·0	0·002474	0·000152	276,300
Castor Oil ..	511·8	·948	485·2	52	64·1	0·003048	0·0002307	225,400
				62	53·5	0·003652	0·0003311	187,300
				72	46·4	0·004210	0·0004403	163,500
				82	40·6	0·004812	0·0005751	142,600
				102	33·3	0·005867	0·0008549	119,300
				122	27·4	0·007131	0·001263	96,600
				142	23·8	0·008208	0·001673	84,900
				162	20·7	0·009437	0·002213	73,200



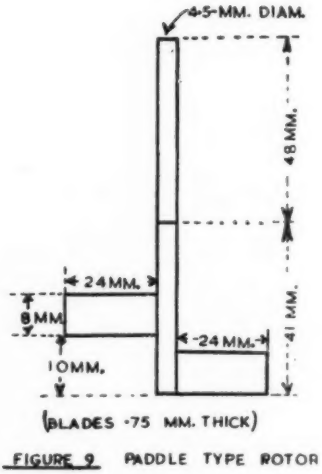


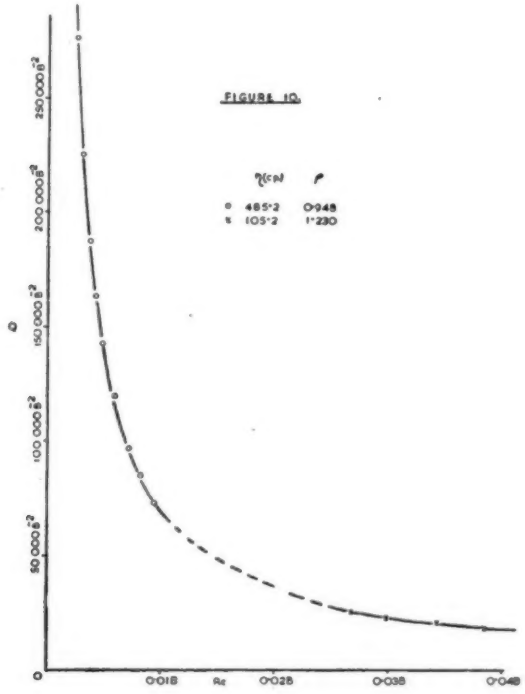
FIGURE 9 PADDLE TYPE ROTOR

In Figure 10 the values of Q and **Re** from Table V were plotted together with a few of the values obtained from Table I. It will be observed that the curve obtained using castor oil appears to be a continuation of the curve previously established using liquids of relatively low viscosity.

As an alternative method for determining the viscosity of a liquid, the mathematical relationship between Q and **Re** may be deternimed from the calibration curve and the corresponding value for Q may be inserted in equation (7). This equation may then be used to calculate the viscosity directly from the rotor speed, driving weight and density values. Clearly, such a procedure would be applicable only to a relatively narrow range of variables if great accuracy is desired. In order to avoid errors, it would be preferable to use the calibration curve directly as previously explained.

While there is no definite evidence available at present, there is reason to believe that changes in the form and size of the test cup holding the liquid are liable to influence the calibration curve. It is important that the testing procedure should not be changed in any way, without checking the calibration curve. It is also desirable to recalibrate the instrument from time to time, particularly when small driving weights are used.

For very accurate work it may be found desirable to limit the rotor speed between predetermined limits. The introduction of correction factors into the relevant equations may also be found feasible and desirable. These aspects are receiving the authors' attention at present.



CONCLUSIONS

The tests described appear to indicate that a relationship between the coefficient of resistance and Reynolds' Number can be determined for a Stormer Viscosimeter for a wide range of viscosities and types of rotor. It appears that the only general equation applicable to the instrument is not expressible in a usable mathematical form and reliable results can be obtained only by making use of calibration curves showing the relationship of Q to **Re** for particular test conditions.

In view of the influence of the Reynolds' Number on the coefficient of resistance, values of "Relative Viscosity" determined as mentioned earlier in this paper are liable to be misleading and this procedure is to be discouraged.

While the present paper is confined to the Stormer Viscosimeter, it is probable that the general principles described are applicable to a number of other types of viscosimeter, principally those which depend on the measurement of the resistance to motion experienced by an object immersed in the liquid to be tested.

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Fuel Research Institute,
Pretoria.

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